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FINGERPRINTING INORGANIC ARSENIC AND ORGANOARSENIC COMPOUNDS IN IN SITU OIL SHALE RETORT AND PROCESS WATERS USING A LIQUID CHROMATOGRAPH COUPLED WITH AN ATOMIC ABSORPTION SPECTROMETER AS A DETECTOR

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and Technology

Fingerprinting Inorganic Arsenic and Organoarsenic Compounds In In Situ Oil Shale Retort and Process Waters Using a Liquid Chromatograph Coupled with an Atomic Absorption Spectrometer as a Detector

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Inorganic arsenic and organoarsenic compounds were speciated in seven oil shale retort and process waters, including samples from simulated, true and modified in situ processes, using a high performance liquid chromatograph automatically coupled to a graphite furnace atomic absorption detector. The molecular forms of arsenic at ppm levels ((μg/mL) in these waters are identified for the first time, and shown to include arsenate, methylarsonic acid and phenylarsonic acid. An arsenic-specific fingerprint chromatogram of each retort or process water studied has significant implications regarding those arsenical species found and those marginally detected, such as dimethylarsinic acid and the suspected carcinogen arsenite. The method demonstrated suggests future means for quantifying environmental impacts of bioactive organometal species involved in oil shale retorting technology.

INTRODUCTION

It is now highly important for our nation to scrutinize all fossil fuel alternatives and develop those that appear promising both commercially and environmentally. Amongst several possibilities, one that emerges as extremely viable is the recovery of shale oil from our substantial domestic deposits of oil shale (1).

Shale oil is recovered from oil shale kerogen by a controlled pyrolysis at 500°C using surface and in situ technologies. These produce, along with the shale oil, considerable amounts of process waters which originate from mineral dehydration, combustion, groundwater seepage, and steam and moisture in the input gas. Since the waters are in intimate contact with raw and partially retorted shale and shale oils, they consitute a leachate of these products (2).

Several possible environmental problems are recognized in the formation and disposal of these retort process products. Firstly, the shale oils and retort waters contain a host of trace organic compounds (2,3) as well as a large array of trace metals and metalloids that are potentially toxic in certain forms to aquatic biota and man (4-6). Secondly, in order to evaluate the latter contaminants for their environmental impacts, the key inorganic and organometallic forms associated with these toxic metals or metalloids (e.g., arsenic, cadmium, mercury, selenium, etc.) must ultimately be identified and their molecular features characterized or speciated (7).

Recent advances, since the introduction (8) of a high performance liquid chromatograph (HPLC) automatically coupled to a graphite furnace atomic absorption spectrometer as a detector (GFAA), permit element-specific characterization of environmentally important trace inorganic and organometallic compounds. These advances provide an effective tool that allows

direct separation and identification of these types of compounds in oil shale process products (8-13). In this paper, we report the successful use of two HPLC-GFAA units (10), in our respective laboratories, to separate and identify inorganic and organic arsenic compounds occurring in oil shale retort and process waters representing current experimental technology.

Arsenic was selected for the present investigations because of its widely acknowledged toxicity in groundwaters (14) and because previous work indicates (3) that total arsenic concentrations in oil shale process waters range from 5 to 15 μg mL^{-1} (ppm) (4).

EXPERIMENTAL

Instrumentation

Two Perkin-Elmer graphite furnace atomic absorption spectrometers, Models 4000 and 460, were used as arsenic-specific detectors for high performance liquid chromatographs (Altex Model 100A), in the respective laboratories. Additionally, each setup had an Altex 153 ultraviolet detector, which was used at 254 nm to monitor the organic matrix and to measure solvent fronts (t_o). Experimental parameters for coupling the HPLC to the GFAA detector, and optimization of arsenic speciation, have been previously described (8-11).

Standards and Oil Shale Retort and Process Water Samples

Inorganic Arsenic and Organoarsenic compounds were purchased from commercial sources and used as obtained. Distilled deionized water (18 MΩ-cm) was produced by a Millipore Corporation Model Milli-Q apparatus and used to prepare all standards and HPLC mobile phases.

Dr. J. Fruchter, Pacific Battelle Northwest Institute, Richland, WA, kindly supplied preserved (at 4°C) Occidental retort and process water samples along with collection histories. Dr. D. Farrier Laramie Energy Technology Center, WY, supplied preserved (at 4°C) Omega-9 retort water. The samples of the

other three retort waters were received from personnel at Laramie Energy Technology Center (150-ton retort water), from Lawrence Livermore Laboratory (L-2), and from Geokinetics, Inc. and were not preserved at 4°C until they reached our laboratories. All samples were maintained at reduced temperature throughout their storage in order to minimize post-collection chemical alterations or volatilization and possible biodegradation by microorganisms (15). Dr. G. J. Olson, National Bureau of Standards, kindly surface plated 0.2 mL of each retort water or process water sample on modified IP medium (low nutrient) at pH 7 or at pH 9.7 plus 5 g L^{-1} NaCl. No growth of aerobic heterotrophic microorganism was evident after a week, consequently, we regarded chemical decomposition as the main possibility of sample degradation.

Seven important in situ oil shale retort and process water samples were examined, including three waters from Occidental's Logan Wash modified in situ process (16) (retort, boiler blowdown, and heater treater waters); Geokinetic's horizontal, true in situ retort water (17); Laramie Energy Technology Center's Rock Springs Site 9 true in situ experiment Omega-9 retort water (18); and two large-scale simulated, modified in situ retort waters: one run, L-2 from Lawrence Livermore Laboratory's 6,000 kg retort (19), and one from Laramie Energy Technology Center's 150-ton retort (20). These materials were warmed to room temperature, filtered (0.45 μm, Millipore), appropriately diluted with deionize water, and directly injected (100-250 μL) into the HPLC-GFAA systems. A summary of the retort and process water sample sources and their respective process features is presented in Table I.

Chromatographic Procedures

Several available (11) gradient compositions were used for the HPLC speciation or arsenicals in the basic (pH ~9.2) retort and process waters, a very effective combination being that of a commercial anion exchange

column (Dionex) with an eluent composition recommended by Woolson and Aharonson (13). This method used a step gradient starting 10 min after injection from 100 percent water-methanol (80:20 v/v) to 100 percent 0.02 M $(NH_4)_2CO_3$ in water-methanol (85:15 v/v) at 5 percent min^{-1}, with a flow rate of 1.2 mL min^{-1}. The HPLC eluent was automatically sampled from a specially designed (8) flowthrough teflon cup for periodic graphite furnace atomic absorption detection at 193.7 nm for arsenic.

Each chromatogram consisted of a series of histogrammic peaks which, in combination, represented an individual eluting chromatographic peak. We then summed the individual histogram comprising each arsenical species peak over the range of $t_R \pm \sigma$ (Table II) to determine total chromatographic peak areas (9,10).

RESULTS AND DISCUSSION

Peak Identification

Figures 1 and 2 compare the arsenic-specific GFAA chromatograms obtained for the seven retort or process waters described. Conventional chromatograms, taken with an ultraviolet (254 nm) detector in series with the GFAA detector, are shown superimposed (solid traces) on the arsenic-selective outputs; these clearly reveal the intensity and complexity of the organic matrix, and the analytical limitations of non-selective detectors. Each time we ran a sample, we also ran five authentic arsenic standards (as 10 ng As in each peak) combined into one solution. These included sodium arsenite, dimethylarsinic acid, methylarsonic acid, phenylarsonic acid and sodium arsenate. We regarded each GFAA chromatographic peak as "positively" identified (Table II) if its retention volume matched that of the mean value of the calibration peak for each As species within two standard deviations

of RSD < 5 percent t_R' (8,9,13). "Tentative" assignments were given to those peaks outlying 2σ, although spiking the field samples with authentic arsenic compounds (see below) yielded the same (increased) single chromatographic peak for both positively and tentatively, identified species.

Moreover, our spiking results confirmed that peak enhancement occurred for only those arsenic compounds spiked, without affecting the peak area of other arsenicals in the matrix. This result is in contrast to other workers (13) who observed a methanol-dependent change in retention time for arsenate when dissolving the sample in methanol. This methanolic arsenate derivative could have interfered with phenylarsonic acid, since it had a similar retention time.

Quantitation of Identified Arsenic Species

The representative figures clearly demonstrate that each retort or process water has a distinctive "fingerprint" and that substantial but variable quantities of arsenate, methylarsonic acid and phenylarsonic acid are present, while arsenite and dimethylarsinic acid are probably absent, or at best, marginally detected. Estimated detection limits and sensitivities for each arsenic species were found to vary, mainly a consequence of the alkaline organic matrix and the fixed GFAA atomization program (9,13). Consequently, we compared each sample chromatogram against that of a standard solution of authentic arsenicals in distilled water. Reliable retention times discused above were obtained this way, as were approximate concentrations of major arsenic species in retort or process waters.

In order to more fully assess matrix effects on t_R and concentrations of minor components, we also ran authentic arsenicals as spikes in several process waters. For example, as shown in Figure 3, in Occidental retort water (diluted 1:10) HPLC-GFAA system detection limits at 95 percent confidence

level (21), using standard additions of 0, 2.5, 5, 10 or 15 ng of analyte were: arsenite, 8.2; dimethylarsinic acid, 20.4; methylarsonic acid, 20.1; phenylarsonic acid, 7.4; and arsenate, 5.2 ng mL^{-1} (as As), respectively. The arsenical concentrations in the Occidental retort water were estimated to be: arsenite, 0.13 ± 0.08; dimethylarsinic acid, 0.049 ± 0.20; methylarsonic acid, 0.096 ± 0.20; phenylarsonic acid, 0.018 ± 0.074, and arsenate, 0.32 ± 0.05 μg mL^{-1}. Clearly from these results and Figure 1 this was a worst-case analysis, although AsO_4^{3-}, and AsO_2^- appeared to give reasonable error limits. For the remaining samples more favorable error limits and concentrations prevailed, as illustrated in Figs. 1 and 2, and summarized in Table III. The neutral arsenical(s) eluting just prior to arsenite undoubtedly interfered with estimations of the latter, but chromatograms obtained with both NBS and LBL instruments suggest that we presently place an upper limit on its presence in the seven sample waters at $< 0.1 \pm 0.06$ ppm; for dimethylarsinic acid, we tentatively place an upper limit of $< 0.05 \pm 0.20$ ppm.

Comparisons Between the Retort and Process Waters

Tables II and III correlate the identified arsenic species and their estimated concentrations with the corresonding retort or process waters. Arsenate is by far the major (0.6-10 ppm) arsenical component identified in all of the samples studied, but the variable concentrations of the other species suggest quantitative diagnostics for monitoring widely different production sites. It is interesting to note that Occidental's retort and process waters (Fig. 1) all contain methylarsonic acid, phenylarsonic acid, arsenate, and one or several neutral or weakly ionized arsenicals, possibly in the molecular R_3As or R_3AsO classes. Generally, neutral or weakly ionized molecules elute with the solvent front (at t_o min) or with only slight retention (at t_R min) in well-behaved ion exchange columns where $k' \sim 1/\mu$; $k' = (t_R - t_o)/t_o$ and μ =ionic strength (23).

The two true in situ retort waters, Geokinetic and Omega-9, also display (Fig. 2) early peaks and contain methyl and phenylarsonic acids, arsenate, and another unknown ionic arsenic species eluting at 20.4 min. Important in a different way, both simulated in situ process waters, 150-Ton and L-2 were distinguished by a significant diagnostic feature involving, respectively, absence of detectable [< 0.002 ppm] phenylarsonic acid in the 150-Ton sample, whereas L-2 water contains > 0.3 ppm of this species. Beyond this, both 150-Ton and L-2 samples contained methylarsonic acid, arsenate, and the neutral component which suggested their similarity to Omega-9. These distinguishable fingerprints may reflect different operating parameters used in the controlled pyrolysis reaction possible with the 150-Ton and L-2 facilities. The similarities last noted may well indicate that basic chemical phenomena are the same in certain laboratory and field retorts, and imply that HPLC-GFAA fingerprinting may serve as a monitoring tool for correlating such operations.

Biogeochemical or Process Origins of Organoarsenicals

The origin of these observed organoarsenic compounds, at this time, is not understood. Kerogen, generally regarded as biogeochemical creation, largely from lipid fractions of ancient algae (2), forms the ubiquitous oil source matrix in shales. Thus, it is conceivable that these methyl- and phenylarsonic acids occur naturally following original biosynthesis or bioaccumulation (6,22) and subsequent mineralization in oil shale and are released with little decomposition upon pyrolysis, ending up as leachates in the process water after intimate contact with the shale oil. Ample evidence is available for both terrestrial and marine biomethylation of inorganic arsenic(V) by modern microorganisms (6,24) and marine algae (6,22) to produce both dimethylarsinate and methylarsonate species; no analogous

biophenylation is reported as far as we know. The negligible amounts of dimethylarsinate or arsenite in our sample waters may result, from oxidative loss of the latter in aged sample (25), or from oxidative pyrolysis of both species in aerobic retorts (5,25), selective rates of formation during original biogenesis, or an alternative purely abiotic synthesis forming methyl- or phenylarsenic bonds in the hot reaction zone of the retort. This last pathway seems quite reasonable for the methylarsonic acid observed, since it parallels the long-known Meyer reaction (26) between alkyl halides and arsenite salts. In boiling aqueous solution both alkylarsonic and dialkylarsinic acids can form, but arylarsonic acids are not similarly obtained (27), thereby suggesting that the phenylarsonic acid observed may arise from other sources. Finally, we cannot rule out formation of these organoarsenic compounds after the retort or process water reaches at the exit of the retort. For example, biomethylated arsenicals could be introduced with boiler feedwater (Occidental boiler blowdown) or by groundwater seepage (28) into *in situ* retorts (Omega-9 and Geokinetic retort waters) and converted to the observed arsonic acids under conditions of high temperatures and pH.

CONCLUSIONS

The significant environmental implications of our study are that potentially toxic inorganic arsenic and organoarsenic compounds in varied mixtures at appreciable concentrations are either released or synthesized during oil shale retorting processes representing present-day technology. The methods applied by us presage similar efforts with other toxic elements. The possibility of their bioaccumulation in soils, water, and edible biota at appreciable distances from the retorting site *via* disposal of retort leachate waters containing bioactive forms may represent potential health

hazards for humans as well as a threat to aquatic species. Suggested bio-leaching of petroliferous shales (29) as an energy-conserving alternative to pyrolysis, must now be regarded with new concerns for re-release or bio-transformation of arsenicals entrapped in kerogen, and this should guide research on other metals as well (24). A more immediate consequence of low-level exposure of workers in these future retort process plants to such inorganic and organoarsenic compounds will require monitoring, since there is not presently a complete understanding of *in vivo* mechanisms of arsenic and other heavy metal toxicity (6).

We believe this to be the first positive molecular characterization of any trace inorganic or organometallic substances in such fossil fuel recovery products. Since the HPLC-GFAA technique is shown to be broadly applicable to a wide variety of elements in many molecular classes, with great freedom from usual matrix interferences (8-13), we envision similar utility for speciating other toxic metal-containing molecules in oil shale products. Among these prospects, mercury, selenium and lead are important because of their known biotransformations (24) and presence in kerogen pyrolysates (5,29). Since the HPLC-GFAA method permits use of a large variety of non-ionic separation columns (8-12), we are also examining the shale oils as well as oil shale kerogens with the aim of establishing the molecular form of hydrophobic or macromolecular organoarsenicals not readily partitioned into retort waters. It is hoped that current qualitative survey work of this type can later offer quantitative bases for optimizing retort process parameters while minimizing impacts of speciated metal toxicants.

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Figure Captions

1. Element-specific chromatograms or arsenic species fingerprints obtained by HPLC-GFAA (bottom of each sample set) and associated UV detector chromatograms (continuous trace shown at top of each set, inverted) are compared against authentic arsenic standards for three water samples taken at different stages of the Occidental Modified In-Situ Process, Retort 6, Logan Wash, Colorado. The chromatogram of the aqueous calibration solution shown at top identifies each of the five arsenicals present at a concentration of 10 ng mL^{-L} (as As).

2. Arsenic fingerprints and corresponding UV chromatograms are compared, as in Fig. 1, against authentic arsenicals for two retort water samples derived from Geokinetics and Omega-9 true in-situ processes.

3. Plots of chromatographic peak areas versus standard additions of individual arsenicals to diluted (1:10) Occidental Retort Water showing relative concentrations.

Table I. Water Types, Sources and Retort Operating Conditions for Samples Used in Arsenic Speciation Study.

Process Water	Retort/ Process	Shale Source	Retorting Atmosphere	Retorting Temperature
SIMULATED IN-SITU RETORTS				
L-2 Retort Water	LLL 6000-kg/ modified in-situ	Anvil Points, Colorado	air/steam	887 °C
150-Ton Retort Water (Run 13)	LETC 150-Ton/ modified in-situ	Anvil Points, Colorado	air	816 °C
FIELD IN-SITU RETORTS				
Omega-9 Retort Water	LETC Site 9/ true in-situ	Rock Springs, Wyoming	air	(a)
Geokinetics Retort Water	Retort 16 true in-situ	Book Cliffs, Utah	air	(a)
Occidental Retort Water	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)
Occidental Boiler Blowdown	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)
Occidental Heater-Treater Water	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)

(a) Field retorting temperatures are not accurately known due to corrosion problems with thermocouples. However, mineral analyses of spent shales from the Geokinetics and Occidental processes suggest temperatures may locally reach 1000 °C.

Table II. Tentative Identification of Inorganic Arsenic and Organoarsenic Compounds by HPLC-GFAA in Various Oil Shale Retort or Process Waters

Sample	Retention Times[a] (min), $t_R \pm \sigma$					
	Sodium Arsenite $NaAsO_2$	Cacodylic Acid $(CH_3)_2As(O)(OH)$	Methylarsonic Acid $CH_3As(O)(OH)_2$	Phenylarsonic Acid ϕ-$As(O)(OH)_2$	Sodium Arsenate Na_3AsO_4	Unknown
CALIBRATION SOLUTIONS[b]	2.1 ± 0.4	16.3 ± 1.8	25.4 ± 0.4	35.7 ± 0.4	44.8 ± 1.1	---
SIMULATED IN-SITU RETORTS[c]						
L-2 Retort Water	---	---	25.2 (+)	35.6 (+)	42.9 (+)	1.0
150-Ton Retort Water	---	---	23.8 (±)	---	43.9 (+)	0.5
FIELD IN-SITU RETORTS[c]						
Omega-9 Retort Water	---	---	25.2 (+)	34.9 (+)	43.7 (+)	1.4 20.4
Geokinetics Retort Water	---	---	26.0 (+)	33.3 (±)	44.5 (+)	1.1 20.4
Occidental Heater-Treater Water[c]	---	---	25.1 (+)	36.4 (+)	46.8 (+)	1.0 14.6
Occidental Boiler Blowdown Water	---	---	24.9 (+)	34.6 (±)	44.2 (+)	0.8
Occidental Retort Water	---	---	24.6 (+)	35.9 (+)	44.8 (+)	0.5 15.0

[a]A dash (---) signifies that the species was not detected. A (±) signifies that the species was tentatively identified. The numerical values are the retention times at which the species or unknown peaks were detected.

[b]Mean ± standard deviation of five or more scattered runs.

[c]Positive identification (+) fell within ± 2σ (2 - 5 % RSD) for calibration runs taken in sequence with unknown runs.

Table III. Estimation of Inorganic and Organic Arsenic Compounds Separated and Detected by HPLC-GFAA Analyses.

Process Water	Compound[a]	$\mu g\ mL^{-1}$[b] (ppm)	
Occidental Retort Water	Unknown organoarsenic compound	-	(-)
	Arsenite	-	(0.13)
	Methylarsonic Acid	0.16	(0.10)
	Phenylarsonic Acid	< 0.003	(0.02)
	Arsenate	0.46	(0.32)
Occidental Heater-Treater Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<2.0	
	Phenylarsonic Acid	<0.42	
	Arsenate	~10	
Occidental Boiler Blowdown Water	Unknown Organoarsenic compound	-	
	Methylarsonic Acid	0.58	
	Phenylarsonic Acid	0.15	
	Arsenate	0.63	
LETC 150-Ton Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<1.5	
	Arsenate	<3.0	
LLL L-2 Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	0.63	
	Unknown inorganic or organo-arsenic compound	-	
	Phenylarsonic Acid	0.31	
	Arsenate	>2.0	
Geokinetic Retort Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<2.0	
	Phenylarsonic Acid	<0.38	
	Arsenate	>10	
LETC Omega-9 Water	Unknown organoarsenic compound	-	
	Methylarsonic Acid	<0.18	
	Phenylarsonic Acid	<0.02	
	Arsenate	<1.6	

[a]Determination of identified compounds by retention times with known authentic compounds, Table 2.

[b]Each standard 10 ng as As. Area under each peak estimated by method of summing peak heights digitized with an integrator (9-11) and comparison with calibration solutions in deionized water or method of additions (22) with spikes in sample solutions (in parentheses).

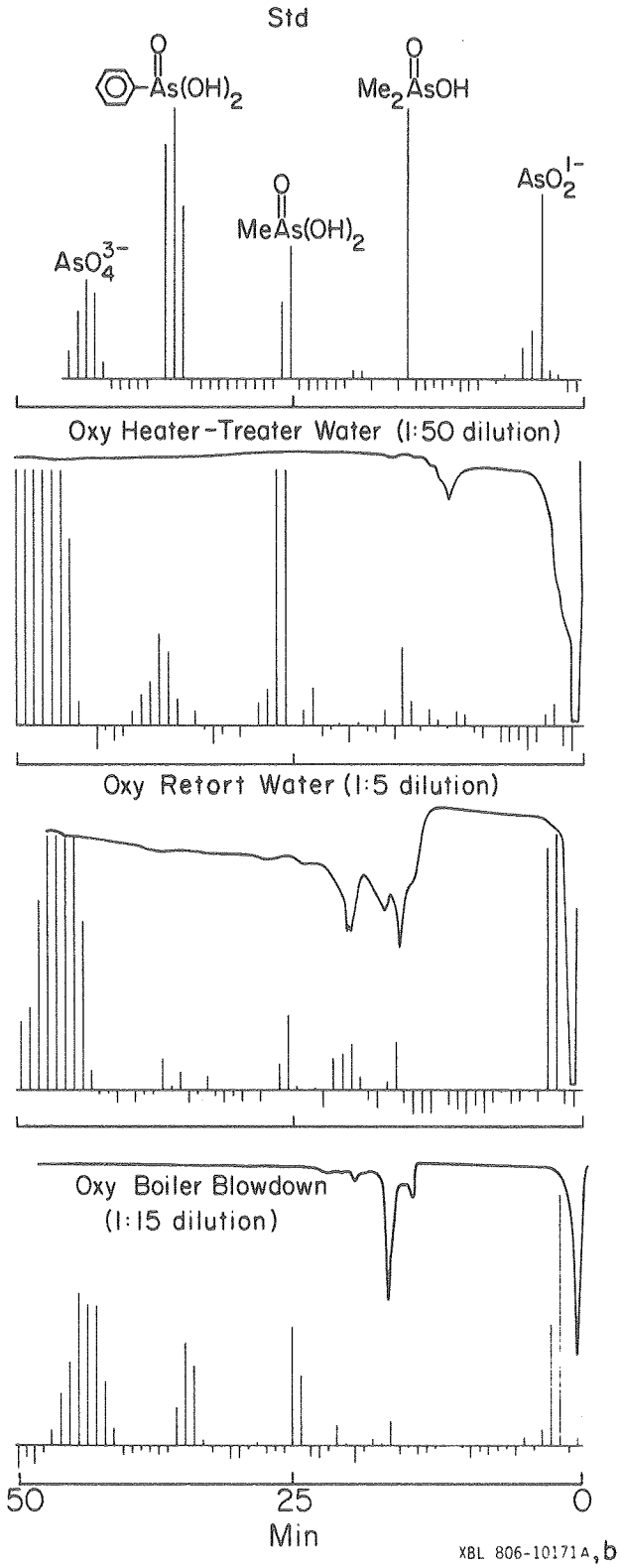
Std
$\bigcirc$-As(OH)$_2$
Me$_2$AsOH
AsO$_4^{3-}$
MeAs(OH)$_2$
AsO$_2^{1-}$
Oxy Heater-Treater Water (1:50 dilution)
Oxy Retort Water (1:5 dilution)
Oxy Boiler Blowdown
(1:15 dilution)
50
25
0
Min
XBL 806-10171A,b

Fig. 1

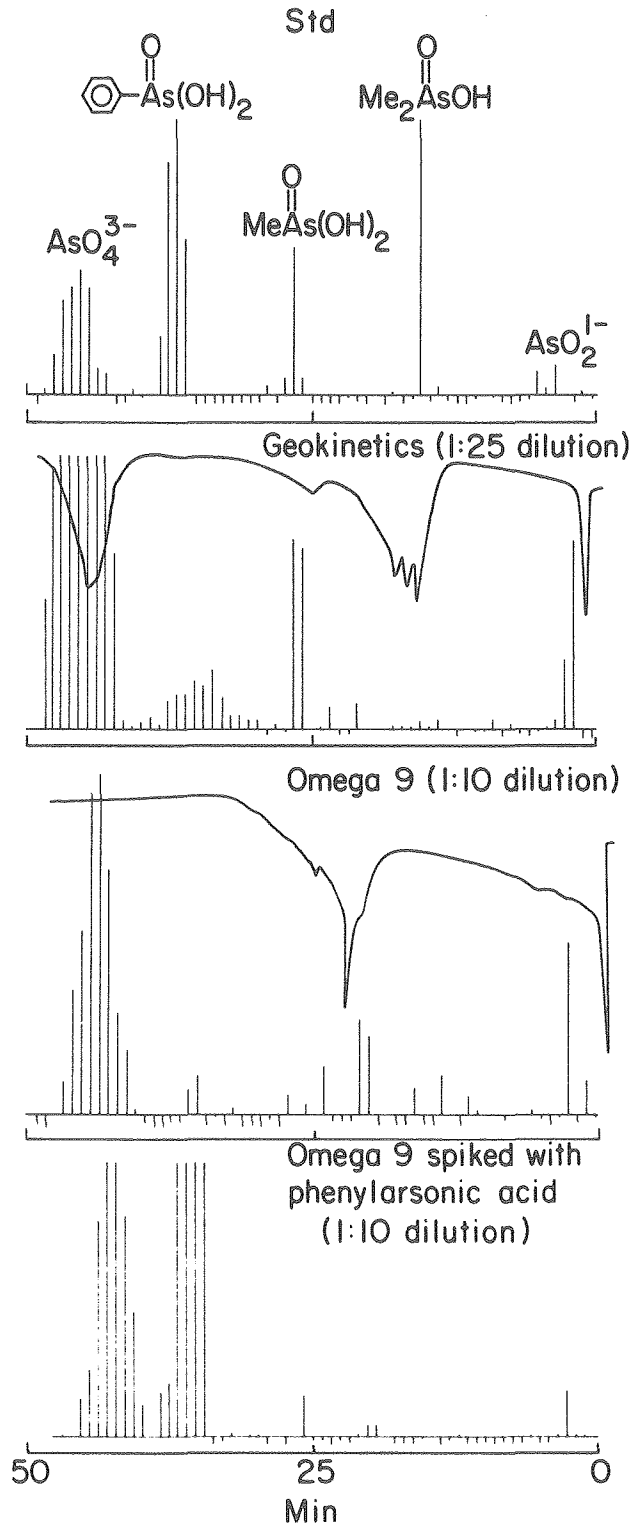

Fig. 2

XBL 806-10168A

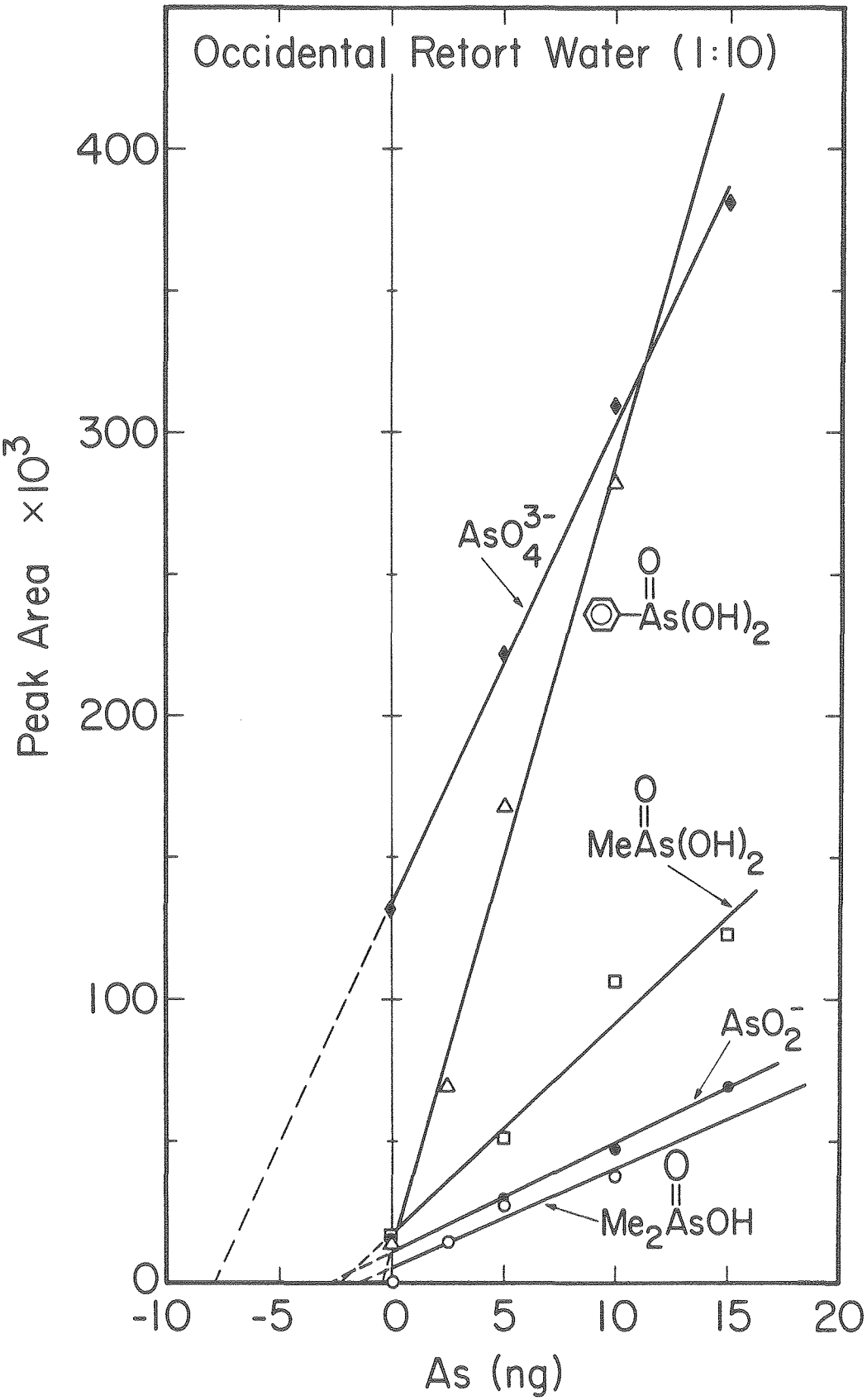

Fig. 3

XBL 816-10279